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(71) Applicant: CRITICAL FLUID SYSTEMS, INC. [US/US]; 25 Acorn Park, Cambridge, MA 02140 (US).

(72) Inventor: MOSES, John, M. ; 105 Vincent Road, Dedham, MA 02026 (US).

(74) Agent: SCHILLER, Robert, J.; 60 Hickory Drive, Waltham, MA 02154 (US).

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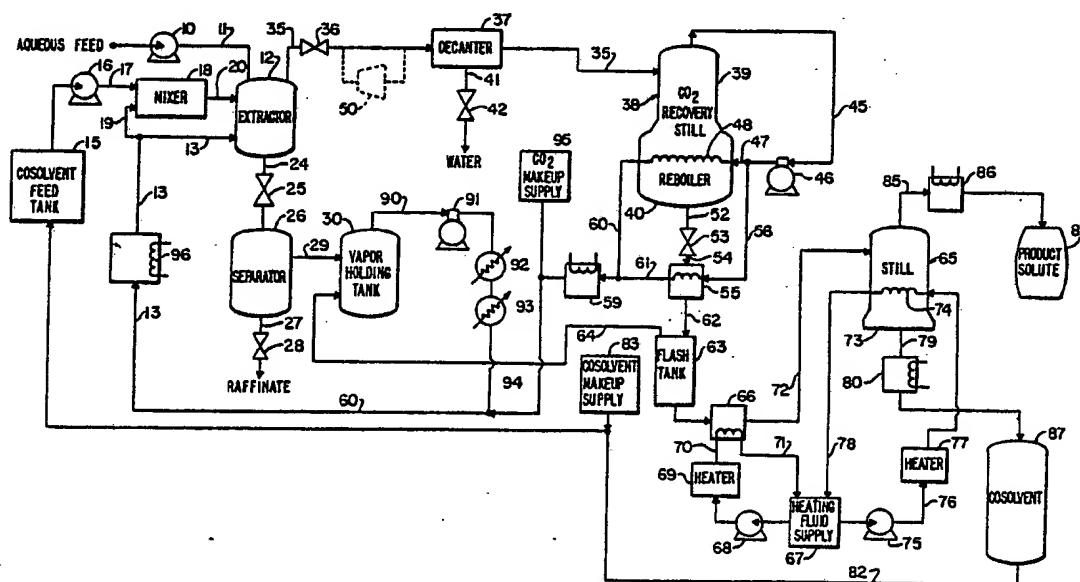
(57) Abstract

A fluid extractant, and a process and apparatus for using the extractant to separate an organic liquid from an aqueous mixture. The extractant comprises a first fluid solvent which is a gas in its near-critical or supercritical state and a cosolvent. A preferred first fluid solvent is near-critical liquid carbon dioxide. Preferred cosolvents are 2-ethyl hexanol for ethanol extraction, and hexanoic acid for acetic acid extraction. Organic compounds such as monohydric alcohols, monoacids, ketones, ethers, aldehydes and esters can be recovered from dilute aqueous solutions more economically than possible by prior art processes of distillation.

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LIQUID CO₂/COSOLVENT EXTRACTION

This invention relates to a process and apparatus for solvent extraction and more particularly to a process and apparatus for extracting large volumes of liquid organics from their aqueous solutions.

5   In a number of commercial processes used for manufacturing many of the high-volume, liquid organic compounds (such as oxygenated hydrocarbons, organic sulfur compounds, organic nitrogen compounds, halogenated hydrocarbons, organo-metallic compounds, and the

10   like) it is necessary to separate the organic compounds from aqueous solutions. In many of these mixtures, water constitutes a major portion of the solution. The separation of these organic compounds from water may require relatively large and complex

15   distillation equipment and demands a heavy expenditure of energy, if only to boil off the water. In a large number of these cases the water and organic liquids form azeotropes, often necessitating higher energy costs to even partially break the azeotrope.

20   At present, about 3% of the total national energy consumption in the United States is used for distillation in petroleum refining and chemical processing. It is therefore clear that a process and/or apparatus which materially decreases the energy requirements for

25   separating even a portion of such solutes from their solutions, would provide a highly desirable savings in energy.

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It is therefore a primary object of this inven-
tion to provide an improved fluid extractant for
extracting an organic solute from its aqueous
solution. A further object is to provide a fluid
5   extractant of the character described which minimizes
the amount of fluid extractant which must be cycled,
and reduces capital equipment and operating costs.
Yet another object is to provide such a fluid extrac-
tant which is particularly suitable for separating
10 from very dilute aqueous solutions, chemicals such
as lower alcohols and acids which are not readily
extracted with a single solvent.

Another primary object of this invention is to
provide an improved process for extracting liquid
15 organic compounds and the like from admixtures with
water. An additional object is to provide such a pro-
cess which makes it possible to employ distillation
equipment having fewer stages in smaller and less
complex distillation equipment than now used. Yet a
20 further object is provide a process for extracting
such organic solutes from their solvents using
liquid carbon dioxide (i.e. near critical or super
critical) as an extractant component, thereby
taking advantage of many of the unique properties
25 of this particular extractant including favorable
diffusion coefficients, low viscosity and low heat
of vaporizaton. A still further object of this

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invention is to provide such a process which uses
as one component of a fluid extractant, a non-
polluting, nontoxic and relatively inexpensive
fluid, i.e. carbon dioxide.

5   Yet another primary object of this invention is
to provide improved apparatus for extracting organic
liquid solutes from their solutions, the improvement
lying in a combination of apparatus components. An
additional object is to provide apparatus of the

10   character described which makes possible the use of a
fluid solvent with resulting savings in energy
requirements and capital equipment costs.

According to one aspect of this invention there
is provided a fluid extractant for extracting an oxy-

15   genated hydrocarbon solute from an aqueous solution,
the extractant comprising a mixture of liquid carbon
dioxide and a cosolvent. The latter preferably has
inter alia, the following attributes: it is a liquid
at the temperature and pressure of the extraction pro-

20   cess, is substantially a better solvent for the hydro-
carbon solute than for water under the extraction
conditions; has a boiling point substantially dif-
ferent than that of the solute, is soluble in the
liquid carbon dioxide to form a single-phase liquid

25   under extraction conditions, and is essentially chemi-
cally unreactive with either the aqueous solution or
the carbon dioxide at process conditions.

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According to another aspect of this invention, there is provided a process for separating an organic liquid solute from an aqueous liquid mixture charac-terized by the steps of contacting at an elevated pressure the liquid mixture with a fluid extractant comprising a first solvent fluid and a cosolvent of the type described, thereby to form two phases, the first phase comprising an extract of the solute in the fluid extractant and the second phase comprising water with residual cosolvent, solute and first solvent; contacting the second phase with additional first solvent fluid to remove the residual cosolvent therefrom and transfer it to said first phase; and separating the first and second phases. The first solvent fluid is a gas under ambient conditions of temperature and pressure which is used in its liquid near-critical or supercritical state. A preferable first solvent fluid is liquid carbon dioxide e.g. car-bon dioxide below its critical temperature and at a pressure sufficiently high to maintain it as a liquid solvent.

According to yet another aspect of this inven-tion, there is provided an apparatus for separating an organic liquid solute from an organic liquid solute/water combination, the apparatus comprising pressure vessel means for effecting countercurrent contact between (1) the combination of an organic

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liquid solute and water, and (2) a pressurized extrac-
tant comprising a mixture of a pressurized first fluid
and a cosolvent of the type described. Because the
latter mixture is a solvent for the organic liquid
5   solute but substantially less for water, the apparatus
produces a fluid extract of the organic liquid in the
extractant fluid and a raffinate comprising water with
minor amounts of the first solvent and organic liquid
solute. The apparatus also comprises mixer means for
10   mixing the first fluid and the liquid cosolvent to
form the extractant fluid; means for introducing the
extractant fluid into the pressure vessel means at a
predetermined level; means for introducing additional
first fluid below the predetermined level; first
15   distillation vessel for separating a still feed into
an overhead vapor and first liquid bottoms and having
associated therewith reboiler means including heat
exchange means for circulating a heat transfer fluid
therethrough in indirect heat exchange relationship
20   with the first liquid bottoms; first pressure line
means connected for conveying the fluid extract as a
still feed from the pressure vessel means to the first
distillation vessel means; vapor compressor means;
second pressure line means incorporating the vapor
25   compressor means and connected for conveying the
overhead vapor to the vapor compressor means and
recompressed vapor therefrom through the heat exchange

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means; third pressure line means for recycling the
condensed vapor or supercritical fluid from the heat
exchange means to the mixer means and to the means for
introducing pressurized first fluid below the prede-
5   termined level; still bottom pressure reducing means;
flash tank means; fourth pressure line means incor-
porating the still bottom pressure reducing means and
connected for conveying the still bottoms from the
reboiler means to the flash tank means through the
10   still bottom pressure reducing means to provide a mix-
ture of the liquid solute and cosolvent; second
distillation vessel means connected for separating the
liquid solute into product and the cosolvent by
distillation; liquid line means incorporating heating
15   means connected for conveying the mixture of the
liquid solute and the cosolvent from the flash tank
means to the second distillation vessel means; and
means for returning the cosolvent from the second
distillation vessel means to the mixer means. In a
20   preferred embodiment of the apparatus, vapor
recompression means are used in connection with the
first distillation vessel to provide the heat required
to heat the still bottoms therein.

Other objects of the invention will in part be
25   obvious and will in part be apparent hereinafter.

The invention accordingly comprises the apparatus
possessing the construction, combination of elements

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and arrangement of parts, the process involving the
several steps and relation of one or more of such
steps with respect to each of the others, and the com-
position of matter having the particular charac-
5   teristics, all of which are exemplified in the
following detailed disclosure and the scope of the
application of which will be indicated in the claims.

For a fuller understanding of the nature and
objects of the invention, reference should be had to
10   the following detailed description taken in connection
with the accompanying drawings in which:

Fig. 1 is a flow chart of the process of the pre-
sent invention using liquid carbon dioxide with a
cosolvent as the extractant fluid;

15   Fig. 2 is a block diagram of an exemplary appara-
tus incorporating the principles of the present
invention;

Fig. 3 is a plot of an exemplary recompression
cycle for carbon dioxide on a fragment of a
20   temperature-entropy diagram for carbon dioxide;

Fig. 4 is a plot showing the relation between the
effectiveness of liquid solute (ethanol) removal from
a water mixture and the amount of cosolvent used in
the process of the present invention; and

25   Fig. 5 is a plot showing the relation between the
calculated distribution coefficient for a given selec-
tivity value for an ethanol/water mixture and the

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amount of cosolvent used.

In the prior art, the removal of highly polar organic compounds, such as the lower alcohols, acids, ethers, aldehydes, ketones, ester and the like, from aqueous streams is often accomplished by steam stripping and fractional distillation. This prior art process requires costly capital equipment and is highly energy intensive. In some cases liquid-liquid solvent extraction may be used for concentrating some feeds. For example, the C_4 to C_{10} esters, ethers and ketones can be used as solvents to extract acetic acid from water; but these solvents have poor selectivities and low equilibrium distribution coefficients, resulting in large solvent circulation rates, excessive equipment size and high energy costs. Moreover, such conventional liquid solvents have high mutual solubilities with water, thus requiring further drying to remove substantial amounts of water.

Recently new processes have been described for recovering acetic acid from feed streams below five weight percent acetic acid. (See for example Ricker, N.L., Pittman, E.F., and King, C.J., "Solvent Properties of Organic Bases for Extraction of Acetic Acid From Dilute Aqueous Industrial Streams," J. Separ. Proc. Technol., $\underline{1}$ (2) 23-30 (1980).) These processes involve using organic Lewis bases such as alkylamines and phosphine oxides as cosolvent extrac-

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tants to increase the distribution coefficients. Such
processes, however, still require the distillation
separation of solvent systems with high-boiling points.
It has been known for some time that many com-
5   pounds which are gases at ambient temperature and
pressure can be converted to supercritical fluids by
subjecting them to conditions such that they are at or
above their critical pressures and temperatures. At
pressures and/or temperatures somewhat below the cri-
10   tical points, most of these gases may be liquefied to
attain what is termed their near-critical state.
These gases in either their near-critical liquid or
supercritical fluid state become good solvents for
many organic materials. It is therefore possible to
15   refer to them as being in a solvent condition, the
actual temperature and pressure for any one fluid in
its solvent condition being readily determinable for
the solute to be separated and recovered.
Among those gases which may be converted to the
20   solvent-condition fluid state are alkane and alkene
hydrocarbons such as ethane, propane, butane, ethy-
lene, and propylene; halogenated hydrocarbons such as
the halomethanes and haloethanes; and inorganics such
as carbon dioxide, ammonia, sulfur dioxide and nitrous
25   oxide. Suitable mixtures of these gases may also be
used.
Of these gases which may be in the solvent con-

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dition, carbon dioxide, ethylene and ethane may be
used as illustrative of the temperatures and pressures
required. These gases are of particular interest
because they fall within the near-critical and
5   supercritical regimes at essentially ambient tem-
perature and have critical pressures in the range of
50 to 75 atmospheres -- pressures which are readily
handled by existing equipment components. The criti-
cal temperature and pressure for each of these gases
10   are well known and, as noted, the solvent condition
temperature and pressure ranges can readily be deter-
mined. For example, carbon dioxide has a critical
temperature of 31.1°C and its solvent condition tem-
perature may range between about -40°C and about 150°C.
15   The critical pressure of carbon dioxide is 72.8
atmospheres and its solvent condition pressure may
range between about 30 and 150 atmospheres, or higher.
Carbon dioxide in its solvent condition is a pre-
ferred first solvent in admixture with a cosolvent in
20   the practice of this invention, for it possesses a
unique combination of properties. In addition to its
good solvent properties under the conditions used,
liquid carbon dioxide in its near-critical state has
distinctly favorable diffusion coefficients compared
25   to normal liquids, a property which gives rise to high
mass-transfer coefficients. This in turn offers the
possibility of minimizing or even effectively elimi-

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nating significant transport resistance in the carbon
dioxide phase resulting in an increase in the overall
extraction rate. It also thereby offers the possibi-
lity of decreasing the size and more effectively opti-
5   mizing the design of the contacting columns used.

A second favorable property of solvent-condition
carbon dioxide is its low viscosity which is about a
factor of ten less than that of conventional liquid
solvents. Since viscosity enters into the flooding
10   characteristics of an extraction column, high flooding
velocities and thus higher flow capacities can be
achieved with a concomitant reduction in contacting
column diameter and capital expenditure costs.

The high volatility of carbon dioxide relative to
15   many of the organic liquids produced and used in high
volume (e.g. ethanol, acetic acid, methyl ethyl
ketone, and the like) and which are generally
extracted from a water mixture, permits a distillation
column in the present invention to operate as an eva-
20   porator with a short stripping section using fewer
stages. The heat of vaporization of the solvent-
condition liquid carbon dioxide is very low, being
about one-fifth of that of many normal liquid solvents
and about one-thirteenth that of water. A low mutual
25   solubility of carbon dioxide in water keeps losses in
the raffinate low and therefore can obviate the need
for a raffinate-stripping column.

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Finally, carbon dioxide is inexpensive, non-polluting and nontoxic, requiring no special equipment or procedures for storage and handling beyond normal practice for pressure systems.

5   The ability of carbon dioxide in its near-critical state and in its supercritical state to serve as an extracting solvent has been known for a number of years. (See for example Francis, A.W., J. Phys. Chem. 58, 1099 (1954) and Ind. Eng. Chem. 47, 230

10   (1955).) Near-critical and supercritical fluids, including carbon dioxide, have been suggested as solvents for a wide range of materials including various oils (U.S. Patents 1,805,751, 2,130,147, 2,281,865); flavor components (U.S. Patent 3,477,856);

15   caffein in coffee (U.S. Patent 3,843,832); cocoa butter from a cocoa mass (U.S. Patent 3,923,847); fats from grains and the like (U.S. Patent 3,939,281); residual hexane from de-fatted grain (U.S. Patent 3,966,981); and a variety of materials such as paraf-

20   fins, glycerol, oils and fats from a variety of compositions (U.S. Patent 3,969,196). A very detailed review of the general field of extraction with supercritical gases is to be found in Angewandte Chemie -- International Edition in English, 17: 10, pp

25   701-784 (October 1978). Of particular interest is the flow sheet of a pilot plant for continuous "destraction" of petroleum top-residues with propane

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appearing as Fig. 5 on page 707 of the Angewandte
Chemie reference.

It must be recognized that the removal of a polar
organic solute from an aqueous solution by solvation
is a complex and unpredictable phenomenon. For
example, it has long been believed that when using a
non-polar solvent to remove a polar organic solute
from water (i.e. the system, solvent/water/solute) the
addition of a cosolvent, more polar than the original
solvent, (i.e. providing the system solvent/cosolvent/
water/solute) should improve the solubility of the
solute in the solvent mixture. As will be seen later
herein, this general rule does not apply where liquid
CO_2 is used as the solvent to remove the organic
solute from aqueous solution.

In U.S. Patents 4,375,387 and 4,349,415, there
are described systems for extracting organic liquids
from their aqueous solution by contacting the solution
with an extractant fluid under conditions of tem-
perature and pressure to render the extractant fluid a
solvent for the organic liquid solute but substan-
tially less for the solvent, thereby forming a fluid
extract of the organic liquid solute in the extractant
fluid and a raffinate comprising the solvent with
minor amounts of the extractant fluid and organic
liquid solute. The extractant fluid is further
characterized as being a gas at ordinary ambient con-

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ditions of temperature and pressure. The fluid
extract of the solute is used to provide a still feed
for a further distillation step. The energy required
to effect distillation is provided by compression of
5   the overhead still vapors to heat the latter and
indirectly heat the still feed. A preferred extrac-
tant used in this system is solvent-condition carbon
dioxide fluid at a pressure between about 30 and about
150 atmospheres and a temperature between about 0° and
10   150°C. The basic energy-saving principle of these
patents is employed in the present invention for the
mixed solvent process.

     Although the use of such extractant fluids as
carbon dioxide, propane, ethylene and ethane
15   (maintained under the specified conditions of tem-
perature and pressure) have been found to be effective
in separating oxygenated hydrocarbons from their
aqueous solutions, some of the liquid organic solutes
such as ethyl alcohol, acetic acid and the like exhi-
20   bit low distribution coefficients and hence require
circulating very large quantities of the liquid
extractant.

     Supercritical carbon dioxide and propane, along
with acetone as an entrainer, have been used to
25   separate mono and diglycerides. The acetone entrainer
increased the solubility of the glycerides, altered
their relative volatilities and facilitated subsequent

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product-solvent separation. (See Peter, Siegfried and
Brunner, Gerd, Angew. Chem. Int. Ed. Engl. <u>746</u>:
46-50 (1978).) Cosolvents to enhance the solubility
and selectivity of materials in the solvent phase of a
5   supercritical carbon dioxide extraction have been pro-
posed in the literature. Zosel (U.S. Patent
3,806,619) discloses the use of water-saturated carbon
dioxide to selectively extract caffein from coffee;
and Wheldon et al (U.S. Patent 4,278,012) mention the
10   use of ethanol to improve hops extraction with carbon
dioxide.

        Shimshick in U.S. Patent 4,250,331 discloses a
process for recovering carboxylic acids from dilute
aqueous solutions of alkali metal salts of the car-
15   boxylic acids by mixing the solutions with a supercri-
tical solution containing carbon dioxide with or with-
out a cosolvent. Shimshick claims that the carbon
dioxide reacts with the salt to form the carboxylic
acid which in turn dissolves in the supercritical
20   fluid. While Shimshick (and Francis in U.S. Patent
4,250,331) recognizes that the use of a cosolvent with
fluid CO_2 may enhance the solvent separation process,
Shimshick teaches that the added cosolvent must be a
supercritical gas having a T_C of less than 130·C, and
25   should be more polar than CO_2 and thus have a net
dipole moment. However, the only cosolvent gases
disclosed by Shimshick are dimethyl ether and a number

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of halogenated hydrocarbons such as the Freons. Francis, on the other hand, discloses a large selection of liquid cosolvents, but is concerned only with extraction from a hydrocarbon mixture, not an aqueous solution.

In the separation of liquid-liquid systems such as aqueous solutions of ethanol, acetic acid, ketones, esters, ethers and the like, using a fluid extractant such as carbon dioxide, it is desirable to be able to maximize the distribution coefficient (D.C.) with respect to the solute, and the selectivity ( ) for the system. The distribution coefficient indicates the ratio of CO_2 to aqueous feed needed for a specified separation, and it is defined, for a particular solute as:

$$D.C. = \frac{(wgt.\ fraction\ of\ solute\ in\ CO_2\ phase)}{(CO_2\text{-free, wgt. fraction of solute in } H_2O\ phase)}$$

The selectivity (β) is a measure of the solute-to-water ratio in the extractant fluid, and it is defined as:

$$\beta = \frac{(weight\ ratio\ solute\ to\ water\ in\ CO_2\ phase)}{(weight\ ratio\ solute\ to\ water\ in\ H_2O\ phase)}$$

In the practice of the present invention, a cosolvent for the solute is added to a first solvent

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fluid (e.g. liquid carbon dioxide), to increase D.C.
and β so that the amount of extractant which must be
cycled is less, and the size of apparatus components
required are smaller than that required for the

5   extractant alone.

        Although supercritical carbon dioxide may be used
as the extractant fluid, it is substantially as effec-
tive in the practice of this invention to use the
carbon dioxide in its liquid state, and preferable to

10   use it at approximately ambient temperature or lower
and at pressures sufficiently near or above its criti-
cal pressure of 72.8 atmospheres to maintain the
liquid in the desired solvent state. A preferred
pressure range is between about 60 and 85 atmospheres.

15   Typical combinations of extraction temperatures and
pressures are illustrated in the following Examples.
For convenience of further description of the inven-
tion, this first or primary solvent fluid will
hereinafter be referred to as liquid carbon dioxide.

20   It is, however, to be understood that gases such as
propane, ethane, ethylene and the like may be used.

        The preferred cosolvent used with the liquid car-
bon dioxide to form the extractant fluid of this
invention is characterized as follows: it is a liquid

25   at about 60°C and standard pressure; it is an oxyge-
nated, monofunctionally substituted hydrocarbon (i.e.
has one radical substituted thereon to impart

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hydrogen-bonding and polar components substantially
lacking in such primary solvents as carbon dioxide);
the cosolvent should have an affinity for and be a
solvent for the organic liquid solute in normal

5   liquid-liquid extraction systems, i.e. the cosolvent
should be a substantially better solvent for the
liquid solute than for the water where an aqueous
solution is to be separated; the cosolvent should have
a solubility in CO_2 greater than 1 weight percent so

10   that under the conditions of extraction and separa-
tion, the carbon dioxide/cosolvent mixture forms a
single phase; the cosolvent should have a distribution
coefficient (CO_2/water) in the absence of solute, of
greater than 3 on a weight basis; the cosolvent should

15   have a boiling point substantially above or below that
of the liquid solute at atmospheric pressure, to faci-
litate a final distillation separation of organic
liquid solute from cosolvent. Finally, the cosolvent
should be substantially chemically unreactive under

20   process conditions with the first solvent fluid, the
liquid solute and water.
        Typically, for example, monofunctional alcohols
having less than six carbon atoms in the molecule,
exhibit distribution coefficients (CO_2/H_2O) of con-

25   siderably less than 3 on a weight basis so are con-
sidered unsuitable as cosolvents in the present
invention.

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The cosolvent is used in an amount sufficient to
effect an appreciable increase in the distribution
coefficient over that achieved by carbon dioxide alone
for a given selectivity (β) of the extraction system
5   being used. Generally, the amount of cosolvent added
to the extraction fluid will not be greater than about
30 weight percent or less than 1 weight percent of the
first solvent fluid, e.g. carbon dioxide, used.
Examples of suitable cosolvents are alcohols such as
10   n-amyl alcohol, 2-ethyl hexanol, n-butanol,
hexanol, ethyl hexanediol, t-amyl alcohol, dodecyl
alcohol, decyl alcohol; acids such as hexanoic acid,
octanoic acid, pentanoic acid, heptanoic acid; amines
such as trioctylamine and isopropylamine; aldehydes
15   such as furfural; phosphine oxides such as trioctyl-
phosphine oxide; and mixtures thereof.
The mixture of first solvent fluid (e.g. liquid
carbon dioxide) and cosolvent is used to extract the
liquid solute from the water. Unless otherwise spe-
20   cified, the term "extractant fluid" is used herein-
after to designate the novel combination of fluids,
of this invention, i.e., liquid carbon dioxide as
representative of the first solvent fluid, and any of
the above-identified cosolvents.
25   The use of cosolvents with liquid CO_2 has been
described in Francis (U.S. Patent 2,631,966) to
fractionate mixtures of lubricating oils. The use of
liquid CO_2 for extraction purposes is also described
in U.S Patents 2,034,495 and 2,346,639 (liquid CO_2 as
cosolvent with SO_2 as primary solvent); U.S. Patent

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2,246,227 (acetone as cosolvent); U.S. Patents
2,281,865 and 2,631,966 (other cosolvents).

The use of extractant fluids according to the
process of this invention is applicable to the extrac-
5   tion of a wide range of organic liquid solutes from
their aqueous solutions, as long as the water of the
solution is relatively immiscible with the extractant
fluid under the conditions of temperature and pressure
employed. Such organic liquid solutes include water-
10   miscible oxygenated hydrocarbons including the alipha-
tic alcohols such as ethanol, isopropanol and the
like; the polyhydric alcohols; as well as acids, alde-
hydes, esters and ketones, and the materials earlier
listed herein.

15   The steps of the process of this invention are
detailed in the flow chart of Fig. 1; and the basic
apparatus is diagrammed in Fig. 2. Reference should
be had to these drawings in the following detailed
description.

20   For purposes of illustration, an aqueous solution
of ethanol will be considered as the feed; and liquid
carbon dioxide as the primary solvent with 2-ethyl
hexanol as a cosolvent will be considered as the
extractant fluid. Fig. 4 illustrates how vapor
25   recompression may be used in separating extract from
the carbon dioxide; and Figs. 5 and 6 illustrate the
improved performance attained with the addition of a

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cosolvent to the extractant fluid through the use of
the process and apparatus of this invention.

Referring to Fig. 2, a feed mixture, for example
ethanol/water, is pressurized and pumped by pump 10

5   through suitable pressure line 11 into extractor 12
designed to provide for the countercurrent contacting
of the aqueous feed mixture and the fluid extractant.
Extractor 12 may be any suitable pressure vessel
designed to provide efficient liquid-liquid contact,

10   such as by countercurrent flow in a packed or sieve-
plate tower. Liquid carbon dioxide from pressure line
13 is introduced into the bottom of extractor 12. The
cosolvent is provided from cosolvent feed tank 15 and
pumped by pump 16 through line 17 into mixer 18 where

15   the cosolvent is mixed with carbon dioxide fed from
line 13 through branch line 19 into mixer 18. Mixer
18 is typically an in-line or static fluid mixer. The
cosolvent/carbon dioxide extractant fluid mixture is
fed through line 20 into extractor 12 at a level which

20   insures that essentially all of the ethanol in the
feed mixture introduced into extractor 12 has been
extracted from the water by the extractant. That por-
tion of additional liquid carbon dioxide which is in-
troduced through line 13 into the bottom of extractor

25   12 serves to extract cosolvent from what may be termed
a preliminary raffinate i.e. the mixture formed in ex-
tractor 12 of water and any residual cosolvent. After

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such extraction, the preliminary raffinate is then
discharged from extractor 12 as essentially cosolvent-
free final raffinate. In a preferred embodiment of
the practice of this invention, the fluid in extractor
5   is maintained at essentially room temperature at a
pressure between about 60 and about 85 atmospheres.

The final liquid raffinate, comprised of water,
some residual carbon dioxide and a very small residual
amount of ethanol and cosolvent, is withdrawn from
10   extractor 12 through line 24 and a pressure-reducing
valve 25 into separator 26. The resulting decompressed
raffinate is a two-phase mixture of liquid water, with
a small amount of dissolved carbon dioxide as well as
the residual ethanol, and carbon dioxide vapor. The
15   water phase is withdrawn through line 27 and pressure-
reducing valve 28 to become the raffinate discharge.
The carbon dioxide forming the vapor phase is trans-
ferred as raffinate vapor flash, at a pressure inter-
mediate that in extractor 12 and atmospheric pressure,
20   from separator 26 by line 29 to a vapor holding tank
30 for subsequent reconversion to liquid carbon
dioxide. The latter is then introduced into the main
stream in line 13.

The liquid carbon dioxide/cosolvent extract con-
25   taining the dissolved ethanol is withdrawn from
extractor 12 under essentially the same conditions as
obtained in extractor 12 and transferred by pressure

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line 35 to the carbon dioxide recovery still 38. In a
preferred embodiment of this invention, particularly
in cases where extractor 12 is operated at the lower
temperatures, e.g. ambient or lower, some reduction
5   of extract pressure is carried out before the extract
is introduced into still 38. This is accomplished in
pressure reducing valve 36 associated with high-
pressure line 35. In line 35, downstream from
pressure reducing valve 36 is a decanter 37 in which
10   small amounts of water in the extract (separated and
coalesced in its pressure reduction) is removed and
periodically drained off through line 41 controlled by
valve 42.

The reduction of pressure, e.g. down to about 50
15   atmospheres, experienced by the carbon dioxide/
cosolvent extract produces a still feed, which is part
liquid, part vapor, at a lower temperature, e.g. from
about 15 to about 20°C. Distillation column 39 of
still 38 is provided with sufficient stages to ensure
20   that essentially all of the ethanol along with the
cosolvent collects in the reboiler 40, along with some
liquid carbon dioxide, to form the still bottoms.

It will be appreciated that these operational con-
ditions are illustrative and not limiting. For
25   example, the carbon dioxide/cosolvent extract pressure
may range from about 15 to about 70 atmospheres prior
to its introduction into distillation column 39; and

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the resulting still feed many range between about 10
and about 25°C.

In keeping with a preferred aspect of this inven-
tion, the heat supplied to reboiler 40 is provided
through out-of-contact or indirect heat exchange with
recompressed carbon dioxide vapor drawn from the
overhead of distillation column 39 and sent through
line 45, compressor 46, and line 47 into heat
exchanger coils 48 in reboiler 40. In an alternative
embodiment, reducing valve 36 may be replaced by a
turbine 50 (shown in dotted lines), the power output
of which may be used to furnish at least a portion of
the power required to drive compressor 46 to which
turbine 50 is mechanically linked by means not shown.

In the apparatus and system illustrated, the
recompression of the carbon dioxide vapor from
distillation column 39 in compressor 46 makes possible
the utilization of the overhead vapor enthalpy as the
reboiler heat source. In order to accomplish this, the
temperature at which the heat is delivered from the
vapor must be raised to provide a driving force for
heat transfer to the still bottoms in reboiler 40.
This is achieved by vapor compression, so that conden-
sation and enthalpy release will occur at a temperature
higher than the boiling point of the reboiler liquid.

A typical vapor-recompression cycle is shown on
the carbon dioxide temperature-entropy diagram of Fig.

3. In this example, the carbon dioxide leaving the
extraction column in admixture with the cosolvent is
at point A, here taken to be 25°C and 65 atmospheres
which means that the extractant is being used in its
5   near-critical liquid state. Upon expansion into the
distillation column, the stream (constituting the still
feed) drops in pressure at constant enthalpy to 50
atmospheres. This is point B which in this example
represents about 22% vapor and 78% liquid at 15°C. In
10   the reboiler, energy is added and liquid is vaporized
to point C, representing all vapor at the same
pressure and temperature. Finally, this vapor,
passing overhead from the distillation column, is then
compressed to point D and, in giving up enthalpy ·in
15   the reboiler, the stream returns from point D to point
A.

        In vapor-recompression evaporation or distilla-
tion, the elevation in boiling point of the more-
volatile component (here carbon dioxide) caused by the
20   presence of the less-volatile component (here the
cosolvent and the liquid organic solute) is important.
The still overhead leaving the distillation column 39
through line 45 will be at or near the boiling point
of the more-volatile component; and the liquid (a solu-
25   tion of the ethanol solute and cosolvent with a minor
amount of liquid carbon dioxide) in reboiler 40 will be
at a higher temperature, the magnitude of the dif-

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ference in temperature depending upon the boiling
point elevation due to the presence of the solute and
cosolvent.

5   The still overhead from distillation column 39 is
compressed adiabatically in compressor 46 to add the
enthalpy which must be transferred to the reboiler
liquid to partially vaporize it while cooling and con-
densing the compressed vapor as it passes through heat
exchanger 48. Thus the mechanism of vapor-
10   recompression distillation requires that the still
overhead must be pressurized by compression to a dew-
point temperature high enough above the reboiler
liquid temperature to provide an economical tem-
peraturedifference driving force to effect the
15   necessary heat transfer within reboiler 40. Therefore
it follows that the greater the boiling-point eleva-
tion due to the presence of the solute and cosolvent,
the greater is the compression required and the
greater is the excess enthalpy that must be added by
20   the compressor to provide an economical temperature-
difference driving force for heat transfer. The
magnitude of this excess may in some cases cause vapor
recompression distillation to be uneconomical.
However, it has been found that there exists an unex-
25   pectedly favorable low value for the boiling-point
elevation in such carbon dioxide/cosolvent/organic
liquid/aqueous solutions as employed in the process of

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this invention. It will, of course, be appreciated
that such a low boiling-point elevation requires only
a moderate increase in still overhead pressure. This
means that a comparatively small amount of energy is
5   required to compress the still overhead and hence to
separate the solute from the liquid carbon dioxide
extract. This, in turn, in part, gives rise to the
low-energy characteristics associated with the pre-
ferred process of this invention.
10   Following the example used to described the embo-
diment of Fig. 2, the still overhead vapor sent to
compressor 46 is under essentially the same con-
ditions, 50 atmospheres and 15·C which typically pre-
vails in distillation column 39; while the compressed
15   and heated vapor introduced into heat exchanger 48 is
at 60 to 85 atmospheres (essentially the extraction
pressure) and about 35 to 45·C. As will be described
below, a portion of the compressed and heated vapor
from compressor 46 may be used to heat the expanded
20   still bottoms from reboiler 40.
            Transfer of heat to the liquid in reboiler 40,
through heat exchange with the compressed and heated
vapors, results in the boiling off of additional car-
bon dioxide. Because of this very low heat of vapori-
25   zation, the heat supplied from the recompressed vapor
is sufficient to boil off the carbon dioxide, a fact
which results in the material reduction in energy

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requirements compared, for example, with the heat
required in the distillation of a liquid organic/water
mixture.

The warmed still bottoms made up of product etha-
5   nol, cosolvent and a small amount of carbon dioxide
are discharged from reboiler 40 through pressure line
52 and pressure-reducing valve 53 from which they
emerge at a much reduced pressure, e.g. 3 atmospheres,
intermediate between the still pressure and atmospheric
10   and at a low temperature, e.g. -10°C. The decompressed
cooled still bottoms are then brought back up to a
temperature, e.g. to about 10°C, intermediate that
temperature at which they were discharged from valve
53 into line 54 and ambient temperature. This heating
15   is accomplished within heat exchanger 55 using a
compressed vapor slip stream drawn off line 47
through line 56 as a heat source. If it is desirable
to have the two streams of carbon dioxide condensate
leaving heat exchanger 48 through line 60 and leaving
20   heat exchanger 55 through line 61 at or near the
extraction temperature, e.g. substantially room tem-
perature, one may include some refrigeration means
such as heat exchanger 59 in line 60 in accordance
with well established engineering practice.
25   The product ethanol and cosolvent along with any
carbon dioxide vapor at the reduced pressure, e.g.
about 3 atmospheres, are carried by line 62 from

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exchanger 55 into flash vessel 63. The latter serves
as a separator from which the carbon dioxide vapor is
taken off through line 64 into vapor holding tank 30.
The liquid mixture bottoms of product and cosolvent in
5   flash tank 63 must be separated and Fig. 2 illustrates
the use of still 65 to accomplish this. The liquid
bottoms are first heated to their boiling point in
heat exchanger 66 through indirect heat exchange with
a heat transfer fluid, e.g. oil taken from a supply
10   tank 67 delivered by a suitable pump 68 through heater
69 by suitable conduit 70 to heat exchanger 66. The
heat transfer fluid discharged from heat exchanger 66
is then returned to supply tank 67 through line 71.
It will be appreciated that the means shown for
15   heating the liquid bottoms discharged from separator
62 are in actuality represented by simplified
illustrations and that many suitable arrangements of
heating means for raising the temperature of the bot-
toms to that required for introduction into still 65
20   through line 72 are within the skill of the art.
The top section of still 65 is equipped in a well
known manner with partial reflux condenser coils (not
detailed in the drawing); the center section has a
feed dispenser and packing of well-known design to
25   provide contact area between the ethanol vapor upflow
and the cosolvent liquid downflow in the distillation
column (not detailed in the drawing); and the bottom

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reboiler section 73 houses reboiler coils 74. Heat is
supplied to the reboiler liquid by circulating a heat
transfer fluid by pump 67 from fluid supply tank 67
through line 76 and heater 77 through coils 74 and
5   returning it by line 78 to supply tank 67.

The bottoms in still reboiler section 73 are the
higher-boiling cosolvent and they are drawn off at a
rate to maintain a liquid-vapor interface just above
the still coils. This cosolvent is taken by line 79
10 through condenser 80 into cosolvent storage tank 81
from where it is recycled through line 82 to cosolvent
feed tank 15. The latter may, if desired, be combined
with tank 81 into a single cosolvent holding tank. If
necessary, makeup cosolvent may be introduced from
15 makeup supply tank 83 into line 82.

The lower-boiling point organic liquid product
vapor is withdrawn from the top of still 65 through
line 85 by way of condenser 86 into product solute
tank 87.

20 The combined carbon dioxide vapor in holding tank
30 must be converted to a solvent condition -- pre-
ferably near or above its critical pressure of 72.8
atmospheres so that it may be used at temperatures
below its critical temperature of 31.1°C. The vapor
25 is therefore taken through line 90 to compressor 91
which is preferably a two-stage compressor with inter-
cooling. Compressor 91 may be mechanically connected

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to turbine 50 (by means not shown) and driven by it.
The heat of compression is subsequently removed from
the compressed carbon dioxide in one or more after-
coolers 92 and 93 prior to being carried by line 94
5   into liquid carbon dioxide return line 60 which
becomes carbon dioxide feed line 13. Any necessary
pressurized makeup solvent-condition carbon dioxide is
brought into feed line 13 from makeup supply 95; and
any required adjustment in carbon dioxide feed tem-
10   perature is accomplished in heat exchanger 96.
In the conventional distillation of azeotrope-
forming mixtures, the resulting product solute may
require additional azeotropic distillation in those
cases in which the product is leaner in solute than
15   the azeotropic composition. In the process of this
invention, however, the fluid solvent and process con-
ditions may be chosen to provide a product solute
which is richer in solute than the corresponding
azeotrope composition, thereby making it possible to
20   eliminate the more difficult and energy-consuming
azeotropic distillation step and to substitute conven-
tional distillation for it. Therefore, in some cases
where sufficient solvent remains in the organic liquid
solute product, it may be desirable to subject the
25   product liquid withdrawn through line 85 to a final
distillation step in conventional distillation appara-
tus (not shown). Such an optional final distillation

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step will, of course, require far less energy than
would be required to effect the separation of the
liquid organic solute and solvent solely by conven-
tional distillation followed by any necessary azeotro-
5   pic distillation.

The individual apparatus components are either
presently available or can be readily designed and
constructed using available information concerning
materials and performance of related available com-
10   ponents. In the case of some of the components it may
be found desirable to use specific embodiments or
modifications of known equipment to achieve an optimum
design balance in the overall system. Thus, for
example, it may be desirable to use a pulsed extraction
15   column to ensure that the small droplets making up the
discontinuous phase are efficiently suspended
throughout the continuous liquid during contacting and
extracting.

The addition of a cosolvent to liquid carbon
20   dioxide extractant is illustrated in Figs. 4 and 5.
The cosolvent used was 2-ethyl hexanol. The fluids in
the extractor 12 (Fig. 2) during extraction were main-
tained between about 15 and 25°C and between about 80
and 82 atmospheres. In carbon dioxide recovery still
25   40 the temperature was maintained between about 10 and
25°C, and pressure between about 35 and 50
atmospheres. The cosolvent/product separation still

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65 was kept at between about 1.5 atmospheres and at a
temperature between about 80 and 170°C.

A number of runs were made in a pilot plant
constructed as a manifestation based upon Fig. 2, and
5   having sampling and analyzing means incorporated in
appropriate locations within the plant. Aqueous solu-
tions having ethanol concentrations varying from as
little as 0.05 weight percent of ethanol to 10+ per-
cent were used as feeds. Solvent-to-feed ratios were
10   varied from 1 to 10, and feed rates of the aqueous
solution were between ½ and 5 pounds per minute. The
amount of cosolvent used was varied from zero up to
about 30 weight percent based on carbon dioxide
weight.

15   The change in the extractor performance due to
the addition of the cosolvent was monitored by
measuring the change in ethanol concentrations in the
raffinate. The results are plotted in Fig. 4 which
shows that the degree of extraction is directly pro-
20   portional to the cosolvent concentration in the liquid
carbon dioxide extractant for a given solvent-to-feed
ratio. This linear relationship extends into dilute
systems which means that suitable cosolvents will work
equally well throughout a commercial extraction
25   column.

A quantitative measure of the extractor perfor-
mance is the stage efficiency. This is calculated

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from an estimate of the number of theoretical stages
required for a given separation and the actual number
of stages. The theoretical number of stages is com-
puted using a McCabe-Thiele diagram. Equilibrium data

5   are needed for alcohol/water/carbon dioxide/cosolvent
systems, and therefore a numerical approximation of
the McCabe-Thiele method was chosen.

The known Kremser-Brown-Souders equation was used
to calculate the number of theoretical stages for the

10   extraction process before the cosolvent addition. An
assumption was made that adding cosolvent to the
extractor would not change the number of theoretical
stages as long as all other operating conditions
remain unchanged. This assumption allowed a new

15   distribution coefficient (D.C.) of ethanol in the pre-
sence of cosolvent to be calculated. The change in
the D.C. was found to increase by as much as a factor
of 20 as shown in Fig. 5. This change signifies that
cosolvents significantly enhance the solvent's

20   stripping action and thus the extraction process.

Using the apparatus and process of the present
invention, it has been found that for the extraction
of ethanol in a CO_2/cosolvent/water/ethanol system, a
desirable cosolvent to be added is 2-ethyl hexanol

25   (typically 2.9% of total volume for a concentration of
about 9% ethanol in the feed). This latter cosolvent
in the proportion indicated provides a DC of from 0.2

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to 0.4. This result can be compared with the DCs
achieved in comparison with other cosolvents or no
cosolvent at all, as shown in the following table
where Wt% is the weight percent of ethanol in the feed
and DC, of course, is the distribution coefficient

TABLE I

	Wt.%	DC
No cosolvent	10	0.03-0.06
hexanol	10	0.1
2-ethyl hexanediol	13	0.01-0.07
n-Amyl alcohol	11	0.12
tert. amyl alcohol	9	0.1
n-butanol	9	0.07

Similarly for the extraction of acetic acid from
a CO_2/cosolvent/water/acid system, hexanoic acid is a
preferred cosolvent because it exhibits a DC of 0.387
for a feed concentration of 10% acetic acid, as com-
pared to other or no solvents as shown in the
following table.

TABLE II

	Wt.%	DC
No cosolvent	10.7	0.164
n-amyl alcohol	9.4	0.281
2-ethyl hexanol	8.7	0.265

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    The addition of cosolvents in extracting an orga-
nic liquid from an aqueous solution using as a fluid
extractant a pressurized gas can decrease the overall
capital and operating costs of an extraction system,
5   decrease the solvent-to-feed ratio required to
perform a given amount of solute stripping, and permits
decreasing the extractor diameter, reboiler surfce
area, compressor capacity and power consumption.
    It will thus be seen that the objects set forth
10   above, among those made apparent from the preceding
description, are efficiently attained and, since cer-
tain changes may be made in carrying out the above
process and in the constructions set forth without
departing from the scope of the invention, it is
15   intended that all matter contained in the above
description or shown in the accompanying drawings
shall be interpreted as illustrative and not in a
limiting sense.

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WE CLAIM:

1   1. A fluid extractant for extracting an organic
2   solute from an aqueous solution, said extractant
3   comprising a mixture of liquid carbon dioxide and an
4   monofunctional hydrocarbon cosolvent, which cosolvent
5   is a liquid at about 60°C and standard pressure; is
6   a substantially better solvent for the liquid solute
7   than for the water; has a solubility in liquid carbon
8   dioxide greater than 1 weight percent that under the
9   conditions of extraction and separation, the carbon
10   dioxide/cosolvent mixture forms a single phase; in
11   the absence of solute, has a distribution coefficient
12   (carbon dioxide/water) of greater than 3 on a weight
13   basis; has a boiling point substantially above or
14   below that of the liquid solute at atmospheric
15   pressure; and is substantially chemically unreactive
16   under process conditions with the first solvent fluid,
17   the liquid solute and water.

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1   2.   A fluid extractant in accordance with claim 1
2   wherein said cosolvent is selected from the group
3   consisting of 2-ethyl hexanol, n-butanol, n-amyl alco-
4   hol, t-amyl alcohol, 2-ethyl hexanol, dodecyl alcohol,
5   decyl alcohol, hexanoic acid, octanoic acid, decanoic
6   acid, pentanoic acid, heptanoic acid, furfural, tri-
7   octylamine, isopropylamine, trioctylphosphine oxide,
8   and mixtures thereof.

1   3.   A fluid extractant in accordance with claim 1
2   wherein said organic liquid solute is ethanol and said
3   cosolvent is 2-ethyl hexanol.

1   4.   A fluid extractant in accordance with claim 1
2   wherein said organic liquid solute is acetic acid and
3   said cosolvent is hexanoic acid.

1   5.   A fluid extractant in accordance with claim 1
2   wherein the temperature of said liquid carbon dioxide
3   is below its critical temperature and is at a pressure
4   sufficient to maintain it in the liquid state.

1   6.   A fluid extractant in accordance with claim 5
2   wherein the temperature of said liquid carbon dioxide
3   ranges between about 15° and about 30°C; and the
4   pressure ranges between about 40 and about 85
5   atmospheres.

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1   7. A process for separating an oxygenated hydro-
2 carbon solute from an aqueous liquid mixture, said
3 process being characterized by the steps of
4   (a) contacting at an elevated pressure said
5 liquid mixture with a fluid extractant comprising a
6 first solvent fluid and a cosolvent thereby to form
7 two phases, the first phase comprising an extract of
8 said solute in said fluid extractant and the second
9 phase comprising water with residual cosolvent and
10 organic solute;
11   (b) contacting said second phase with additional
12 first solvent fluid to remove said residual cosolvent
13 therefrom and transfer it to said first phase; and
14   (c) separating said first and second phases; said
15 first solvent fluid being a gas under ordinary ambient
16 conditions of temperature and pressure as to render it
17 a fluid which is substantially more solvent for said
18 solute than for the water of said mixture;
19   said cosolvent being a monofunctional
20 hydrocarbon that is a a liquid at about 60·C and
21 standard pressure; is a substantially better solvent
22 for the liquid solute than for the water; has a solu-
23 bility in carbon dioxide greater than 1 weight percent
24 so that under the conditions of extraction and separa-
25 tion, the carbon dioxide/cosolvent mixture forms a
26 single phase; in the absence of solute, has a distri-
27 bution coefficient (carbon dioxide/water) of greater
28 than 3 on a weight basis; has a boiling point substan-

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29 tially above or below that of the liquid solute at
30 atmospheric pressure; and is substantially chemically
31 unreactive under process conditions with the first
32 solvent fluid, the liquid solute and water.

1   8. A process in accordance with claim 7 wherein
2   said first solvent fluid is carbon dioxide.

1   9. A process in accordance with claim 8 wherein
2   said carbon dioxide is at a temperature below its cri-
3   tical temperature and is at a pressure sufficient to
4   maintain it in the liquid state.

1   10. A process in accordance with claim 7 wherein
2   said oxygenated hydrocarbon liquid solute is a mono-
3   hydric alcohol, monoacid, ketone, aldehyde, ether or
4   ester.

1   11. A process in accordance with claim 7 wherein
2   said oxygenated hydrocarbon liquid solute is ethanol,
3   said first solvent fluid is liquid carbon dioxide and
4   said cosolvent is 2-ethyl hexanol.

1   12. A process in accordance with claim 7 wherein
2   said oxygenated hydrocarbon solute is acetic acid,
3   said first solvent fluid is liquid carbon dioxide and
4   said cosolvent is hexanoic acid.

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1   13. In a process for separating an oxygenated
2   hydrocarbon liquid solute from an aqueous liquid mix-
3   ture, in which process the mixture is contacted with
4   an extractant fluid comprising a first solvent fluid
5   which is a gas under ordinary ambient conditions of
6   temperature and pressure but which is under such con-
7   ditions of temperature and pressure as to render it a
8   fluid which is substantially more solvent for said
9   solute than for the water of said mixture, the impro-
10   vement wherein
11   said extractant fluid also comprises a cosolvent
12   which is a liquid at about 60°C and standard pressure;
13   is a substantially better solvent for the liquid
14   solute than for the water; has a solubility in liquid
15   carbon dioxide greater than 1 weight percent so that
16   under the conditions of extraction and separation, the
17   carbon dioxide/cosolvent mixture forms a single phase;
18   has a distribution coefficient (carbon dioxide/water)
19   in the absence of solute, of greater than 3 on a
20   weight basis; has a boiling point substantially above
21   or below that of the liquid solute at atmospheric
22   pressure; and is substantially chemically unreactive
23   under process conditions with the first solvent fluid,
24   the liquid solute and water; and
25   said improvement further comprises the steps of:
26   forming a fluid extract of said liquid solute in
27   said extractant fluid, and a raffinate comprising
28   substantially water;

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29   separating said fluid extract and said raffinate;
30   distilling said fluid extract to separate same
31 into a still overhead fraction comprising substan-
32 tially said first solvent fluid, and a bottoms frac-
33 tion comprising substantially said cosolvent and said
34 liquid solute; and
35   distilling said bottoms fraction to separate same
36 into said liquid solute and said cosolvent.

1   14. A process in accordance with claim 13
2 wherein said first solvent fluid is carbon dioxide.

1   15. A process in accordance with claim 14
2 wherein said carbon dioxide is liquid at a temperature
3 below its critical temperature and at a pressure suf-
4 ficient to maintain it in the liquid state.

1   16. A process in accordance with claim 13
2 wherein said oxygenated hydrocarbon liquid solute is a
3 monohydric alcohol, monoacid, ketone, aldehyde, ether
4 or ester.

1   17. A process in accordance with claim 13 wherein
2 said oxygenated hydrocarbon liquid solute is ethanol,
3 said first solvent fluid is liquid carbon dioxide and
4 said cosolvent is 2-ethyl hexanol.

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1   18.   A process in accordance with claim 13
2   wherein said oxygenated hydrocarbon liquid solute is
3   acetic acid, said first solvent fluid is liquid carbon
4   dioxide and said cosolvent is hexanoic acid.

1   19.   A process in accordance with claim 13 in
2   which said step of forming a fluid extract of said
3   liquid solute comprises the steps of contacting said
4   aqueous liquid mixture with said extractant fluid to
5   form said fluid extract and said raffinate and
6   further contacting said raffinate with an additional
7   quantity of said first fluid solvent to remove any of
8   said cosolvent therefrom for addition to said fluid
9   extract.

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1   20. A process for separating an oxygenated

2 hydrocarbon liquid solute from a mixture of said

3 solute and water, said process comprising the steps of

4   (a) contacting said mixture with an extractant

5 fluid under conditions of temperature and pressure to

6 render said extractant fluid a solvent for said orga-

7 nic liquid solute but substantially less for water,

8 thereby forming a fluid extract of said liquid solute

9 in said extractant fluid and a preliminary raffinate,

10 said extractant comprising

11   (1) a first solvent fluid which is a gas

12 under ordinary ambient conditions of temperature

13 and pressure but which is under such conditions

14 of temperature and pressure as to render it a

15 fluid which is substantially more solvent for

16 said solute than for the water of said mixture,

17 and

18   (2) a cosolvent which is a mono-

19 functionally substituted hydrocarbon that is a

20 liquid at standard temperature and pressure; is

21 a substantially better solvent for the liquid

22 solute than for the water; has a solubility in

23 liquid carbon dioxide greater than 1 weight per-

24 cent so that under the conditions of extraction

25 and separation, the carbon dioxide/cosolvent mix-

26 ture forms a single phase; has a distribution

27 coefficient (carbon dioxide/water) in the absence

28 of solute, of greater than 3 on a weight basis;

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29   has a boiling point substantially above or below

30   that of the liquid solute at atmospheric

31   pressure; and is substantially chemically unreac-

32   tive under process conditions with the first

33   solvent fluid, the liquid solute and water;

34   (b) contacting said preliminary raffinate under

35   the conditions obtaining during said contacting step

36   (a) with additional first solvent to remove cosolvent

37   from said preliminary raffinate to form a final raf-

38   finate and to add said cosolvent thus removed to said

39   fluid extract;

40   (c) separating said fluid extract and said final

41   raffinate;

42   (d) providing said fluid extract as a first

43   still feed separable into two phases by distillation;

44   (e) distilling said first still feed to produce

45   a first still overhead vapor of said first solvent

46   fluid and liquid still bottoms comprising said

47   cosolvent and said liquid solute;

48   (f) flashing said still bottoms to form a second

49   still feed;

50   (g) distilling said second still feed to

51   separate said cosolvent for recycling and said liquid

52   solute as product; and

53   (h) adjusting the temperature and pressure of

54   said first still overhead vapor of said first solvent

55   fluid before mixing it with said cosolvent to form

56   said extract fluid.

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1   21. A process in accordance with claim 20
2 wherein said step of adjusting said temperature and
3 pressure of said first still overhead vapor comprises
4 compressing said vapor to provide compressed vapor at
5 an elevated temperature and effecting indirect heat
6 exchange between said compressed vapor and said liquid
7 still bottoms to provide thermal energy required in
8 step (e), and to form a liquid condensate of said
9 vapor.

1   22. A process in accordance with claim 20
2 wherein said first solvent fluid is carbon dioxide.

1   23. A process in accordance with claim 22
2 wherein said carbon dioxide is liquid at a temperature
3 below its critical temperature and at a pressure suf-
4 ficient to maintain it in the liqiud state.

1   24. A process in accordance with claim 20
2 wherein said oxygented hydrocarbon liquid solute is a
3 monohydric alcohol, monoacid, ketone, aldehyde or
4 ester.

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1   25. A process for separating an oxygenated
2   hydrocarbon liquid solute from an aqueous mixture,
3   said process comprising the steps of
4   (a) contacting said mixture with an extractant
5   fluid comprising liquid carbon dioxide and a
6   cosolvent, wherein said cosolvent is a liquid at about
7   60·C and standard pressure; is a monofunctionally
8   substituted hydrocarbon; is a substantially
9   better solvent for the liquid solute than for
10   the water; has a solubility in the liquid carbon
11   dioxide greater than 1 weight percent so that
12   under the conditions of extraction and separation, the
13   carbon dioxide/cosolvent mixture forms a single phase;
14   has a distribution coefficient (carbon dioxide/water)
15   in the absence of solute, of greater than 3 on a
16   weight basis; has a boiling point substantially above
17   or below that of the liquid solute at atmospheric
18   pressure; and is substantially chemically unreactive
19   under process conditions with the liquid carbon
20   dioxide, the liquid solute and water;
21   said contacting being carried out at a pressure
22   above about 75 atmospheres and a temperature below the
23   critical temperature of carbon dioxide, thereby
24   forming a fluid exctract of said solute and a prelimi-
25   nary raffinate comprising water with minor amounts of
26   said carbon dioxide and said cosolvent;
27   (b) contacting said preliminary raffinate under
28   the conditions obtaining in step (a) with liquid car-

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29   bon dioxide to remove cosolvent from said preliminary
30   raffinate to form a final raffinate and to add said
31   cosolvent thus removed to said fluid extract of said
32   solute and said extractant fluid;

33   (c)   separating said fluid extractant from said
34   final raffinate;

35   (d)   reducing the pressure of said fluid extract
36   to form a first still feed separable into two phases
37   by distillation;

38   (e)   distilling said first still feed to produce
39   a first still overhead comprising essentially all car-
40   bon dioxide vapor and first still bottoms comprising
41   said solute and said cosolvent;

42   (f)   recompressing said carbon dioxide vapor from
43   step (e) to provide recompressed carbon dioxide at a
44   pressure essentially equivalent to that of said carbon
45   dioxide used in step (a) and at a temperature above
46   the boiling point of said still bottoms;

47   (g)   effecting indirect heat exchange between
48   said recompressed carbon dioxide and said first still
49   bottoms to provide thermal energy required in said
50   distilling step (e) and to form a carbon dioxide
51   liquid condensate;

52   (h)   flashing said liquid still bottoms by
53   further reducing their pressure to remove residual
54   carbon dioxide as vapor flash and to form a second
55   still feed;

56   (i)   heating said second still feed to the

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57   boiling point and distilling it to separate said
58   cosolvent and said liquid solute as product;
59   (j)   adjusting, if necessary, the temperature of
60   said carbon dioxide liquid condensate; and
61   (k)   mixing the recovered cosolvent from step (i)
62   and said carbon dioxide from step (g) for recycling in
63   the process.

1   26.   A process in accordance with claim 25
2   including the steps of
3   (1)   reducing the pressure of said final raf-
4   finate to a level intermediate between that of said
5   contacting step and atmospheric and separating the
6   resulting carbon dioxide vapor flash from the final
7   liquid raffinate;
8   (m)   combining said carbon dioxide vapor flashes
9   from steps (h) and (1);
10   (n)   adjusting the pressure and temperature of
11   the combined vapor flashes of step (m) and adding the
12   resulting liquid carbon dioxide to said liquid carbon
13   dioxide of step (g).

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1   27. Apparatus for separating an organic liquid
2   solute from an organic liquid solute water mixture,
3   said apparatus comprising in combination
4   (a) pressure vessel means for effecting counter-
5   current contact between (1) a mixture of an organic
6   liquid solute and water and (2) a pressurized extrac-
7   tant fluid comprising a mixture of a pressurized fluid
8   and a liquid cosolvent, said mixture being a solvent
9   for said organic liquid solute but substantilly less
10 for said water, to produce a fluid extract of said
11 organic liquid in said extractant fluid and a raf-
12 finate comprising water with minor amounts of said
13 first fluid;
14   (b) mixer means for mixing said first fluid and
15 said liquid cosolvent to form said extractant fluid;
16   (c) means for introducing said extractant fluid
17 into said pressure vessel means at a predetermined
18 level;
19   (d) means for introducing additional first fluid
20 below said predetermined level;
21   (e) first distillation vessel means for
22 separating a still feed into an overhead vapor and
23 first liquid bottoms having associated therewith
24 reboiler means including heat exchange means for cir-
25 culating a heat transfer fluid therethrough in
26 indirect heat exchange relationship with said first
27 liquid bottoms;
28   (f) first pressure line means connnected for

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29   conveying said fluid extract as a still feed from said
30   pressure vessel means to said first distillation
31   vessel means;
32   (g)   vapor compressor means;
33   (h)   second pressure line means incorporating
34   said vapor compressor means and connected for con-
35   veying said overhead vapor to said vapor compressor
36   means and recompressed vapor therefrom through said
37   heat exchange means;
38   (i)   third pressure line means for recycling said
39   recompressed vapor from said heat exchange means to
40   said mixer means and to said means to introduce
41   pressurized first fluid below said predetermined level;
42   (j)   still bottom pressure reducing means;
43   (k)   flash tank means;
44   (l)   fourth pressure line means incorporating
45   said still bottom pressure reducing means and con-
46   nected for conveying said still bottoms from said
47   reboiler means to said flash tank means through said
48   still bottom pressure reducing means to provide a mix-
49   ture of said liquid solute and said cosolvent;
50   (m)   second distillation vessel means for
51   separating said liquid solute as product and said
52   cosolvent by distillation;
53   (n)   liquid line means incorporating heating
54   means and connected for conveying said mixture of said
55   liquid solute and said cosolvent from said flash tank
56   means to said second distillation vessel means; and

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57   (o)   means for returning said cosolvent from said
58   second distillation vessel means to said mixer means.

1   28.   An apparatus in accordance with claim 27
2   comprising
3   (p)   raffinate separating means for providing a
4   vapor flash of said first fluid;
5   (q)   vapor flash collection means;
6   (r)   means connected for conveying first fluid
7   vapor from said raffinate separating means and from
8   said flash tank means to said vapor flash collection
9   means;
10   (s)   means for adjusting the temperature and
11   pressure of said vapor from said vapor flash collec-
12   tion means to that in said third pressure line means;
13   and
14   (t)   means for introducing the resulting
15   temperature/pressure-adjusted fluid into said third
16   pressure line means.

1   29.   An apparatus in accordance with claim 27
2   including fluid extract pressure reducing means asso-
3   ciated with said first pressure line means.

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1   30.   An apparatus in accordance with claim 29
2   including coalesced liquid decanting means associated
3   with said first pressure line means and downstream
4   from said pressure reducing means.

1   31.   An apparatus in accordance with claim 29
2   wherein said fluid extract pressure reducing means
3   comprises energy generating means.

1   32.   An apparatus in accordance with claim 31
2   wherein said energy generating means are mechanically
3   linked to said vapor compressor means to provide power
4   thereto.

1   33.   An apparatus in accordance with claim 27
2   including fifth pressure line means connecting said
3   second and third pressure line means and having
4   supplemental heat exchange means arranged for
5   effecting heat exchange between a slip stream of said
6   recompressed vapor and said still bottoms.

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1   34. An apparatus in accordance with claim 27
2   wherein said second distillation vessel means incor-
3   porates reboiler means and includes heat exchange
4   means associated with said reboiler means arranged for
5   heating said cosolvent forming said still bottoms of
6   said second distillation vessel means.

1   35. An apparatus in accordance with claim 27
2   including condenser means arranged for separately
3   cooling and condensing said liquid solute product and
4   said cosolvent from said second distillation vessel
5   means.

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FIG. 1

SUBSTITUTE SHEET
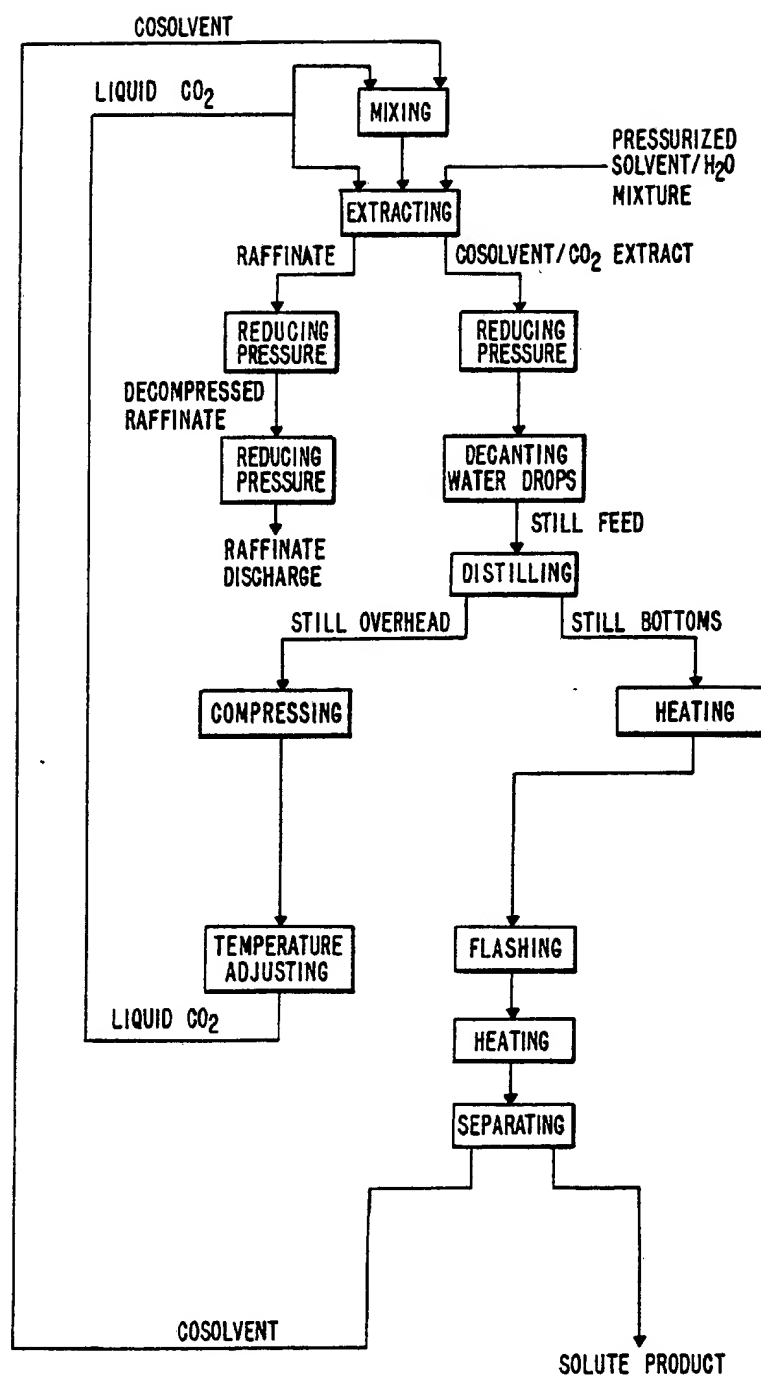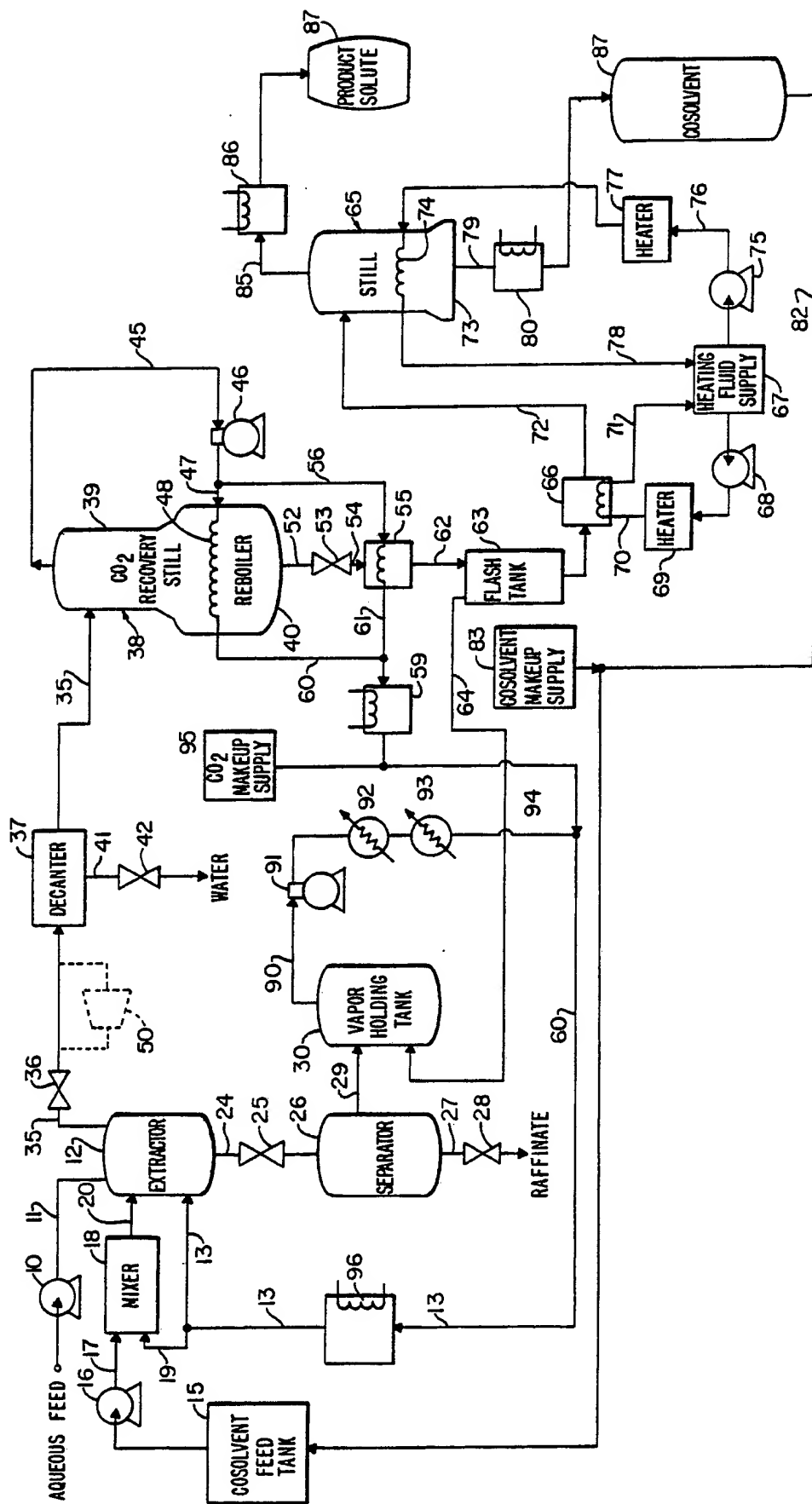
FIG. 2
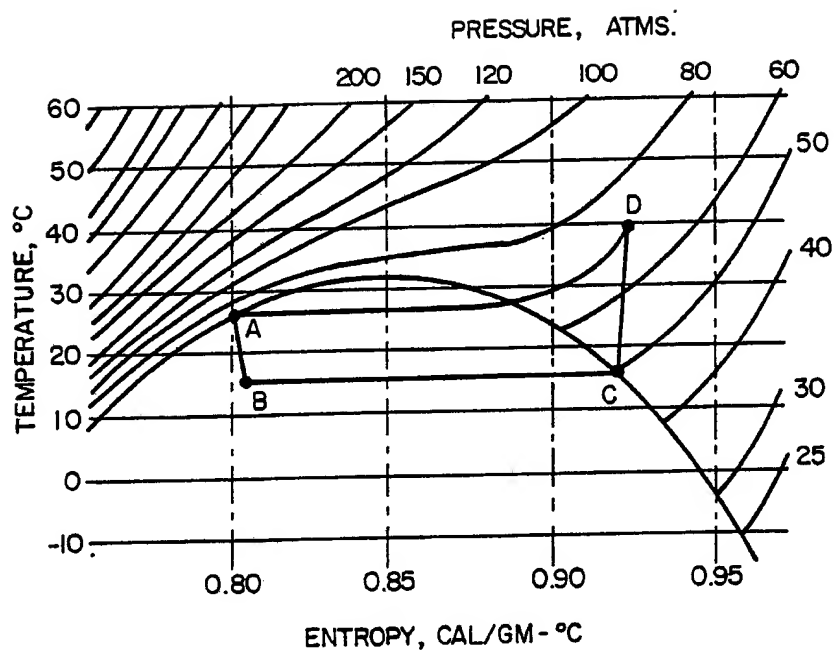
APPROXIMATE CO₂ STATE CONDITIONS

    A- IN EXTRACTION COLUMN

    B- FEED TO STILL

    C- OVERHEAD FROM STILL

    D- COMPRESSOR DISCHARGE

FIG. 3
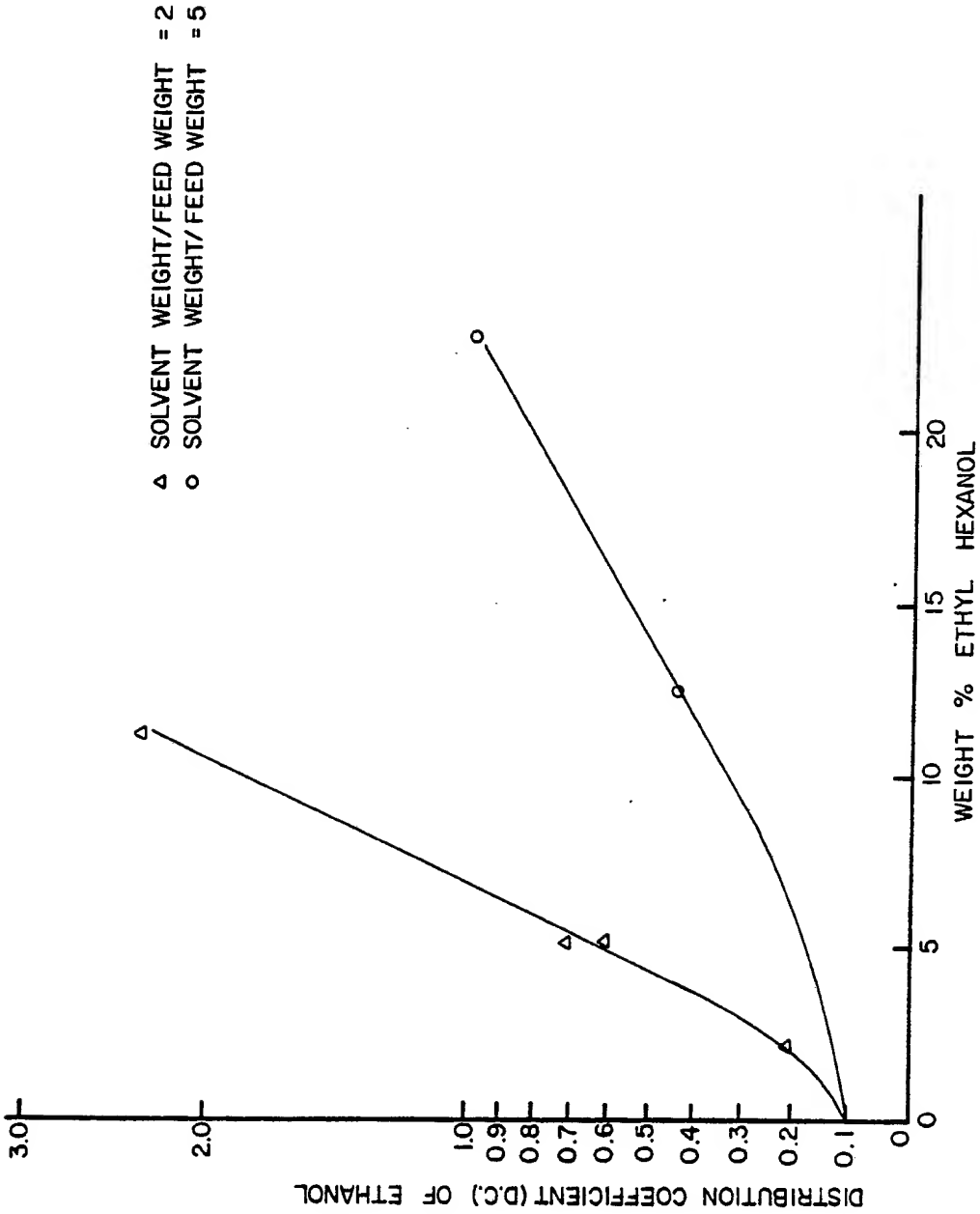
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FIG. 4

FIG. 5

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL ^{3} B01D 11/04
U.S. CL. 210/634

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols	
US	203/16, 19 210/634 562/608	568/913

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category*	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	US,A, 4,349,415, PUBLISHED 14 SEPTEMBER 1982, DEFILIPPI ET AL.	1-35
Y	US,A, 4,353,784, PUBLISHED 12 OCTOBER 1982, KOGA ET AL.	1-35
Y	US,A, 4,401,514, PUBLISHED 30 AUGUST 1983, KANZLER, ET AL.	1-35
P Y	US,A, 4,455,198, PUBLISHED 19 JUNE 1984, ZUDKEVITCH ET AL.	1-35

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [3]	Date of Mailing of this International Search Report [2]
9 MAY 1985	2 0 MAY 1985

International Searching Authority [1]	Signature of Authorized Officer [10]
ISA/US	FRANK SPEAR

Form PCT/ISA/210 (second sheet) (October 1981)